ENABLING HIGH-ENERGY, HIGH-VOLTAGE LITHIUM-ION CELLS FOR TRANSPORTATION APPLICATIONS: MATERIALS CHARACTERIZATION

Project ID: BAT254

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Argonne National Laboratory
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2018 DOE Vehicle Technologies Office Annual
Merit Review

OVERVIEW

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2018
- Percent complete: 94%

Budget

- Total project funding:
  FY17 $4.0M
- BAT252, BAT253, and BAT254
  (ANL, NREL, ORNL, LBNL)

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  – Cost
  – Performance
  – Safety

Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

PROJECT OBJECTIVES - RELEVANCE

To understand the interfacial structures and reactions that lead to electrolyte/surface instabilities in nickel-rich electrodes for high energy density lithium-ion batteries and how these limitations limit implementation into transportation technologies.

- **Development and utilization of surface sensitive characterization tools** to determine the interfacial phases that make up the electrochemically active surface of Ni-rich cathodes**.**

- **Metal Oxide coatings -** Investigate how coating methodology and electrochemical cycling affect the longevity and performance of inorganic coatings on Ni-rich cathodes.

- **Evaluate thin film cathodes** under the HE-HV protocols to establish a baseline system to aid in the evaluation of electrolyte additives.

Any proposed future work is subject to change based on funding levels

MILESTONES

(Q1) Relationship of manganese cations in the bulk and coating quality (*completed*)

Understand the effect of bulk transition metal composition on coating performance. Why does the effectiveness of an Al_2O_3 coating track the Mn concentration for Ni-rich cathodes.

(Q2) Relationship of form of alumina and coating quality (*completed*)

Depending on annealing temperature the alumina coating can be at the surface, as alumina, surface lithiated oxide, or diluted into the bulk (e.g. 811, LCO).   When cycling - identify the most effective alumina-based coating for a coated Ni-rich cathode.

(Q3) Method of coating synthesis as a function of stoichiometry

Summarize the effect of Al_2O_3 coating conditions (precursor, solvent, heat treatments and cathode composition) on electrochemical performance of Ni-rich cathodes

Go/No-Go – Can the low initial capacity seen for alumina coated samples made using an aqueous process be overcome and controlled?

(Q4) Correlate coating formation process to electrochemical performance

Develop an understanding on interface evolution, composition and surface changes with high energy cycling for nickel rich cathodes
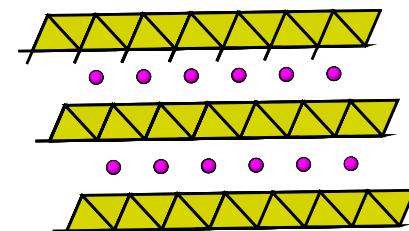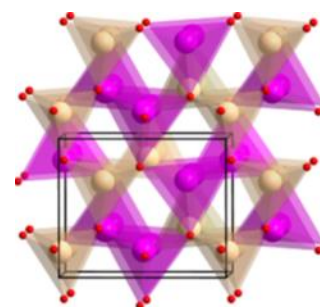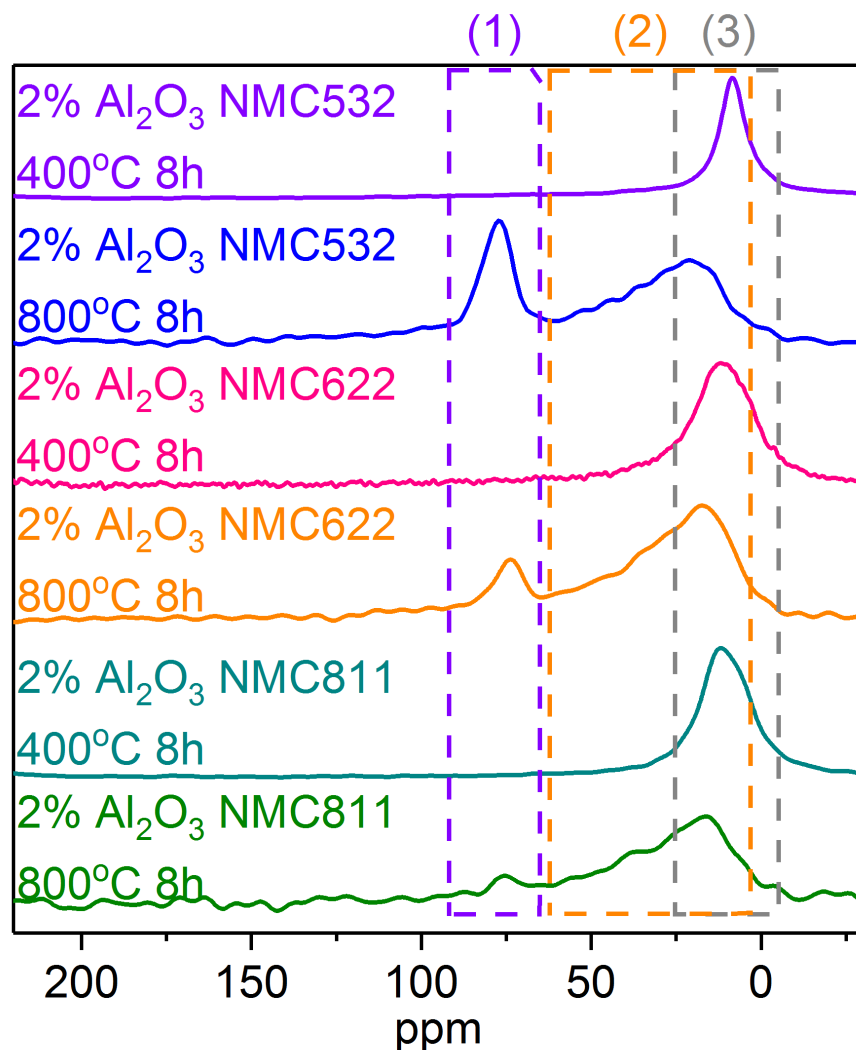
APPROACH

Approach: Devise materials strategies, utilize spectroscopic tools, and create electrochemical models that allow us to better understand the limitations and breakdown mechanisms of high voltage-high energy cathodes in a lithium-ion battery cell configuration.

Strategy: Several phenomena contribute to the gradual breakdown in performance of lithium-ion batteries including surface degradation, cathode instability, reactivity with organic electrolyte components, and surface films. Utilizing NCM or NCA materials as baseline systems –

1. Investigate the effects of interfacial coatings on the stability, structure, and performance of NMC or NCA cathodes
2. Utilize a combination of single crystal NMC materials and theory to identify the most stable facets towards reduction.
3. Correlate materials processing and sample history with electrochemical performance to develop a better understanding of the electrode-electrolyte interface.

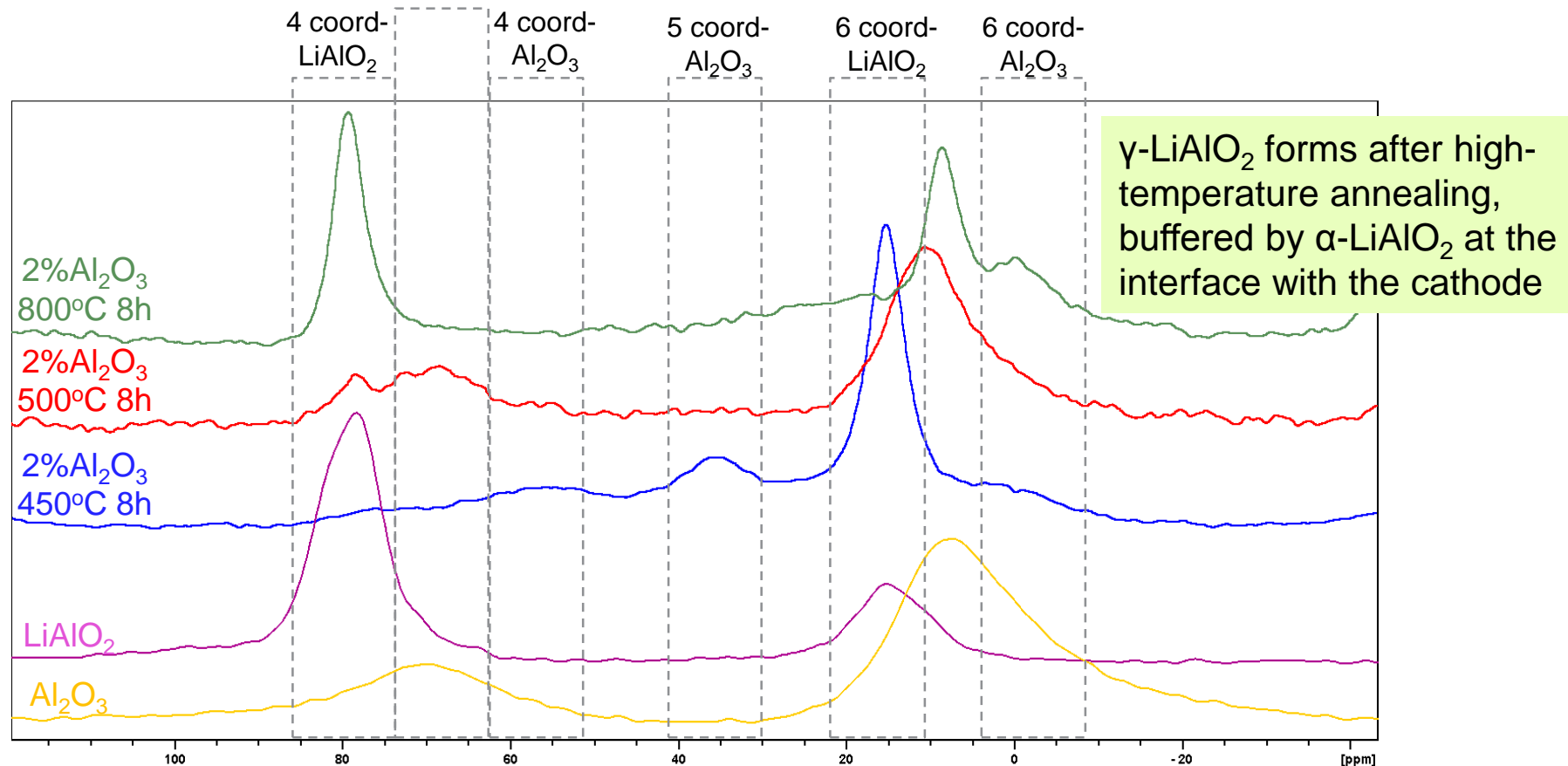# EFFECT OF CATHODE COMPOSITION ON SURFACE/ INTERFACE AND BULK: ^{27}Al NMR

(1) (2) (3)

2% Al_2O_3 NMC532
400°C 8h

2% Al_2O_3 NMC532
800°C 8h

2% Al_2O_3 NMC622
400°C 8h

2% Al_2O_3 NMC622
800°C 8h

2% Al_2O_3 NMC811
400°C 8h

2% Al_2O_3 NMC811
800°C 8h

ppm

γ-LiAlO$_2$

α-LiAlO$_2$

As the amount of Mn in the NMC decreases, the surface coating layer changes withy decreasing free Al_2O_3 (or α-$LiAlO_2$) thus diminishing the amount of γ-$LiAlO_2$ that can form at high temperature.

(1) 4-coordinate γ-LiAlO$_2$
(2) 6-coordinate α-LiAlO$_2$
(3) 6-coordinate Al_2O_3 or $Al(OH)_3$

SURFACE STRUCTURE CHANGES WITH ANNEALING TEMPERATURE ^{27}Al MAS High Resolution NMR at 19.96T

4 coord- γ LiAlO$_2$ at boundaries

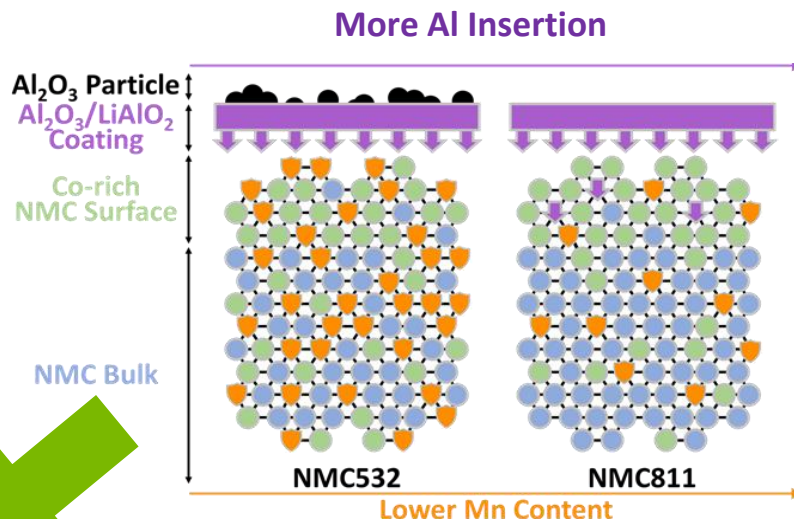- **6-coordinate α-LiAlO$_2$ forms at ~450 °C**
- **4-coordinate γ-LiAlO$_2$ forms at ~500 °C**

4 coord-LiAlO$_2$

4 coord-Al$_2$O$_3$

5 coord-Al$_2$O$_3$

6 coord-LiAlO$_2$

6 coord-Al$_2$O$_3$

γ-LiAlO$_2$ forms after high-temperature annealing, buffered by α-LiAlO$_2$ at the interface with the cathode

2%Al$_2$O$_3$ 800°C 8h

2%Al$_2$O$_3$ 500°C 8h

2%Al$_2$O$_3$ 450°C 8h

LiAlO$_2$

Al$_2$O$_3$

EFFECT OF CATHODE COMPOSITION SURFACE AND BULK

Doped and coated/doped samples have different Al local environments

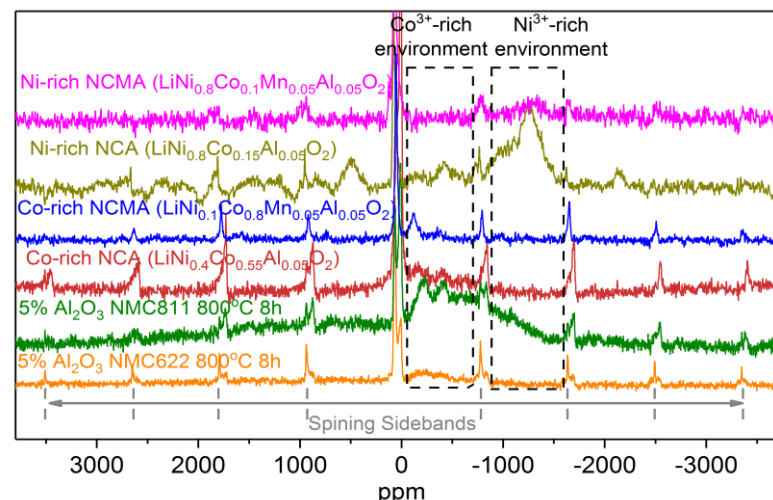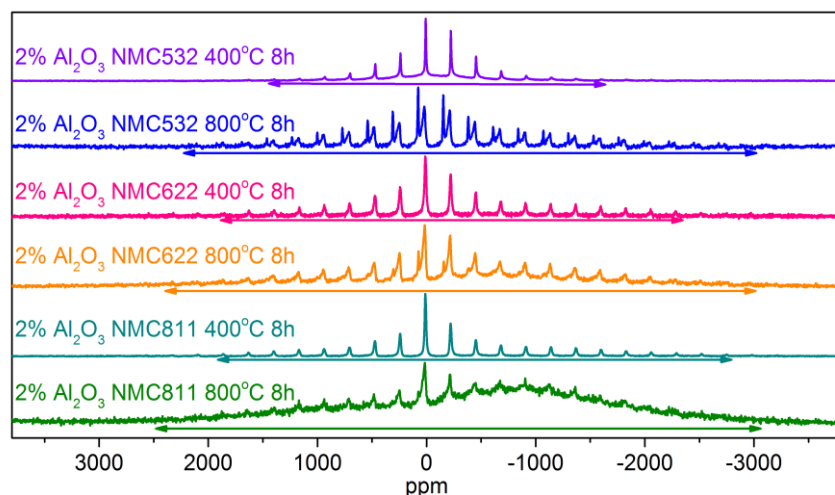**For low Mn NMCs** *like 811* - the surface alumina moves with high-temperature annealing to become an Al^{3+} lattice dopant

More Al Insertion

Al_2O_3 Particle
$Al_2O_3/LiAlO_2$ Coating
Co-rich NMC Surface

NMC Bulk

Ni

Co

Mn

Al

NMC532   NMC811

Lower Mn Content

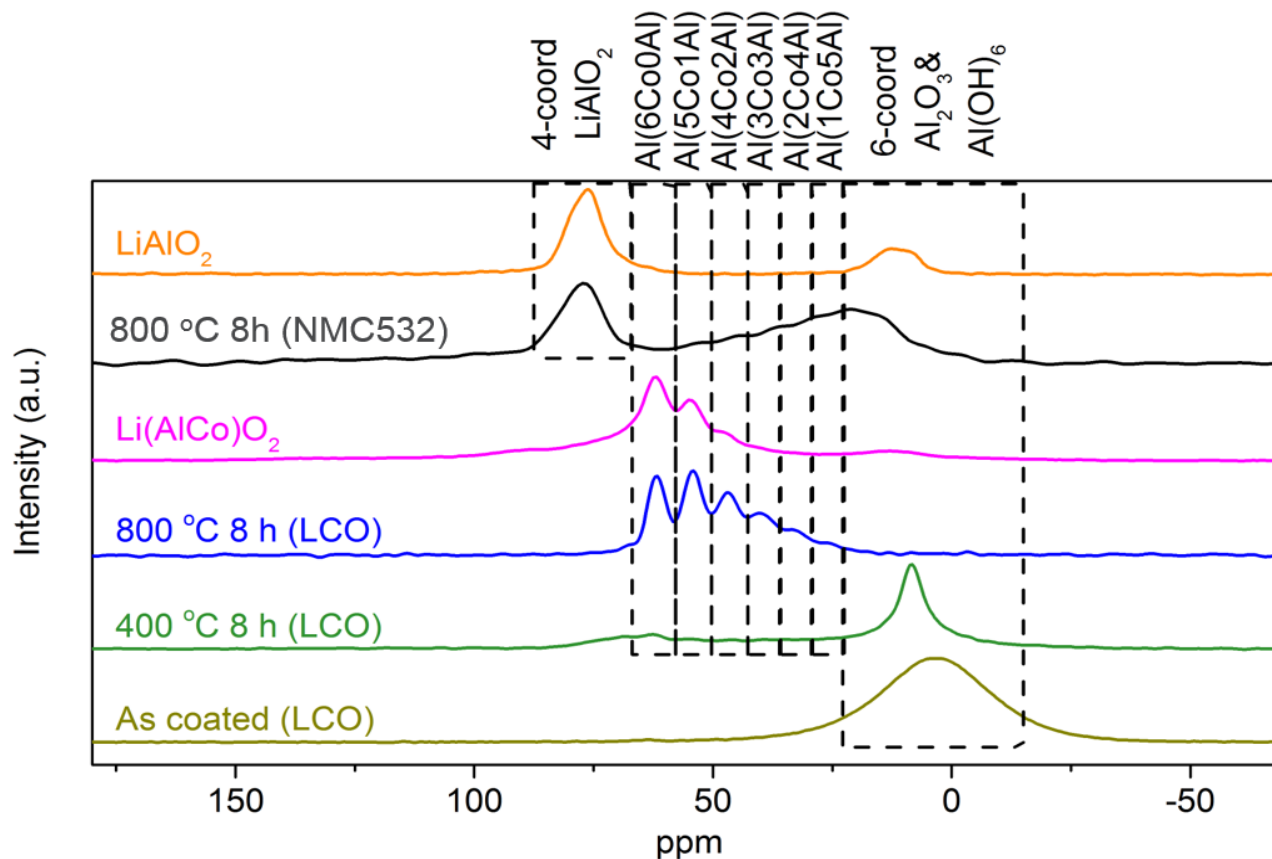**Coated NMC 811 and 622** have Al1Ni, Al2Ni, Al3Ni coordination environments

NCA and Al doped NMC 811 have Al5Ni, and Al6Ni coordination environments

There is no evidence of Mn-Al coordination

2% Al_2O_3 NMC532 400°C 8h
2% Al_2O_3 NMC532 800°C 8h
2% Al_2O_3 NMC622 400°C 8h
2% Al_2O_3 NMC622 800°C 8h
2% Al_2O_3 NMC811 400°C 8h
2% Al_2O_3 NMC811 800°C 8h

ppm

Co^{3+}-rich environment Ni^{3+}-rich environment

Ni-rich NCMA ($LiNi_{0.8}Co_{0.1}Mn_{0.05}Al_{0.05}O_2$)
Ni-rich NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$)
Co-rich NCMA ($LiNi_{0.1}Co_{0.8}Mn_{0.05}Al_{0.05}O_2$)
Co-rich NCA ($LiNi_{0.4}Co_{0.55}Al_{0.05}O_2$)
5% Al_2O_3 NMC811 800°C 8h
5% Al_2O_3 NMC622 800°C 8h

Spining Sidebands

ppm

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BERKELEY LAB

Argonne NATIONAL LABORATORY

# AL$_2$O$_3$ COATINGS: LCO IS SIMILAR TO 811

- Significant differences exist between LCO (with d^6 Co(III)) and NMC cathodes (with more than 16% Mn) when coated with Al$_2$O$_3$ and annealed.

- For these Ni-rich cathodes - ^{27}Al NMR data shows the Al(III) remains on the surface and is segregated as LiAlO$_2$ and/or Al$_2$O$_3$, while for 811 and LCO, the Al(III) is in the lattice surrounded by the TM cations.

EFFECT OF CATHODE COMPOSITION ON SURFACE
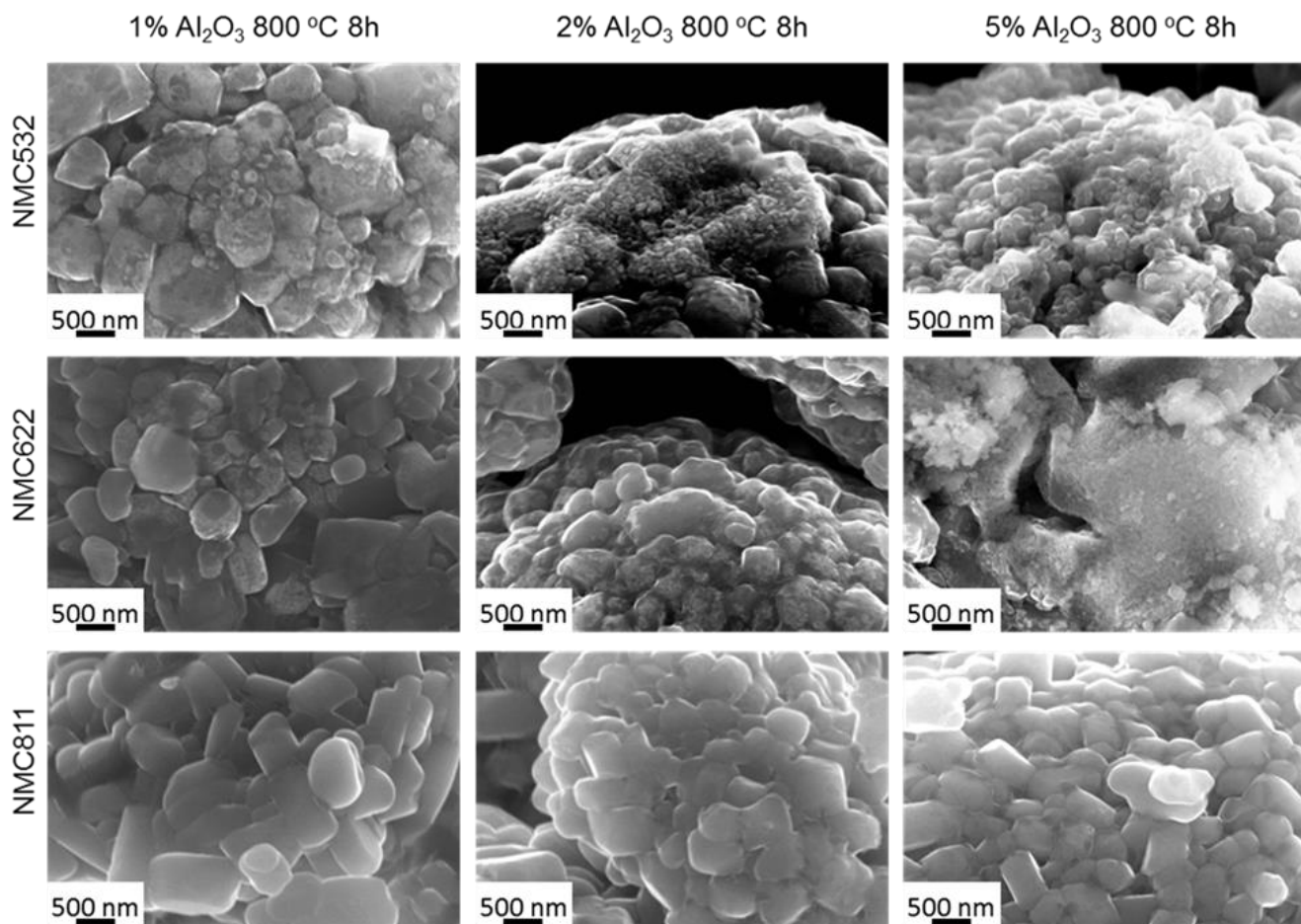
- **Dense crystalline coating forms after high temperature annealing**

- **Loose amorphous coating formed on at lower temperatures**

Less Mn content → More Al diffusion into lattice → smoother surface with less scattered particles

EFFECT OF CATHODE COATING THICKNESS

- Thinner Al_2O_3 coating brings higher capacity

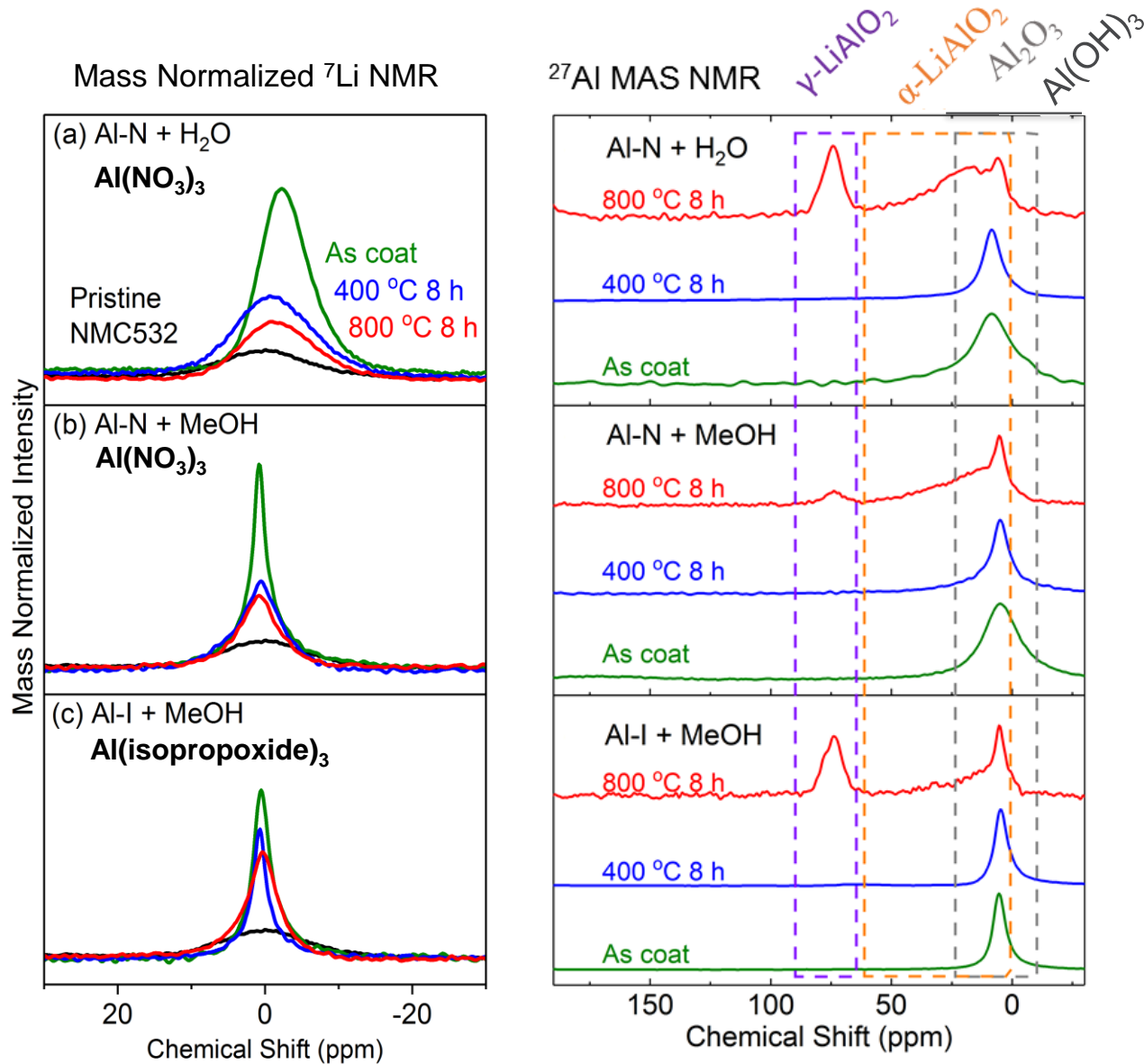- Al diffusion leads to poor cycle life – in contrast to the results seen for $Li(CoAl)O_2$
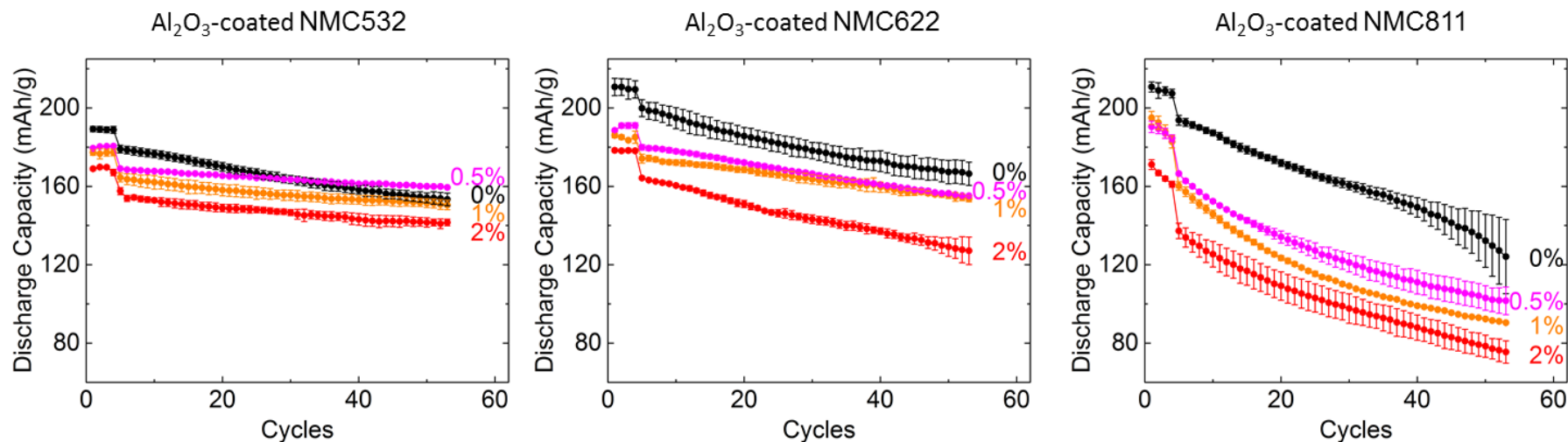
Anode: Li metal. Cycled at C/10 for 4 cycles and then C/3 for 50 cycles

Method: aqueous coating; Aluminum Nitrate coating precursor annealed at 800 °C 8h
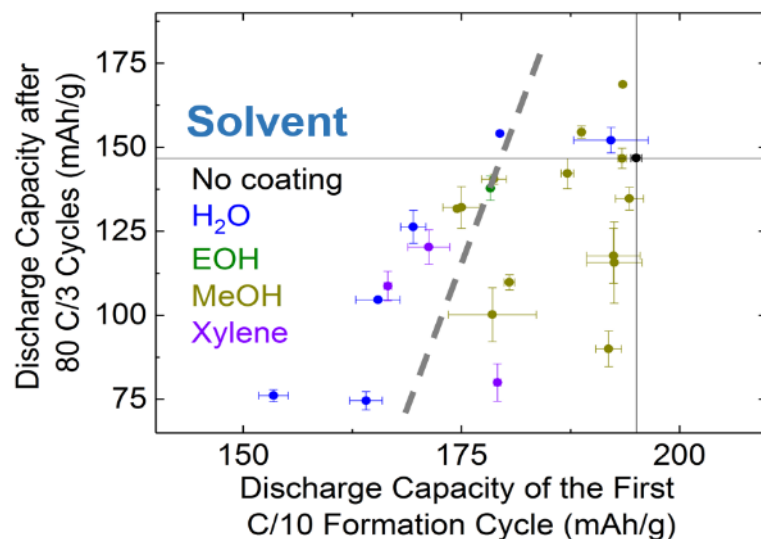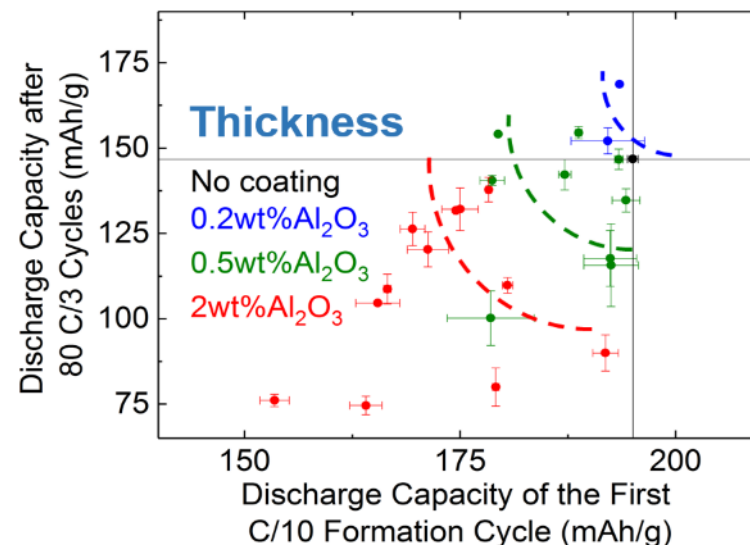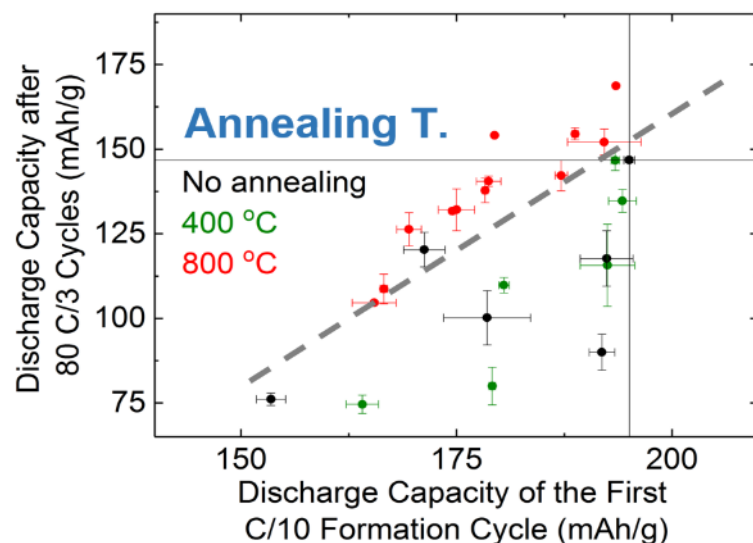
Aluminum local environment and coordination in the lattice can effect the electrochemical performance

EFFECT OF SALT AND SOLVENT

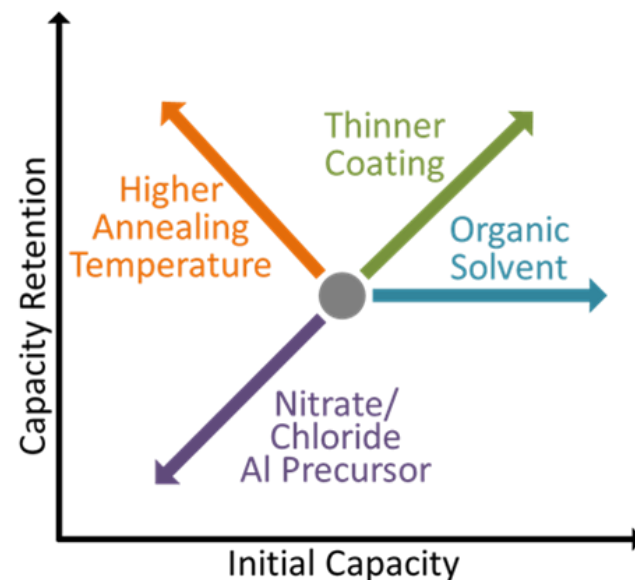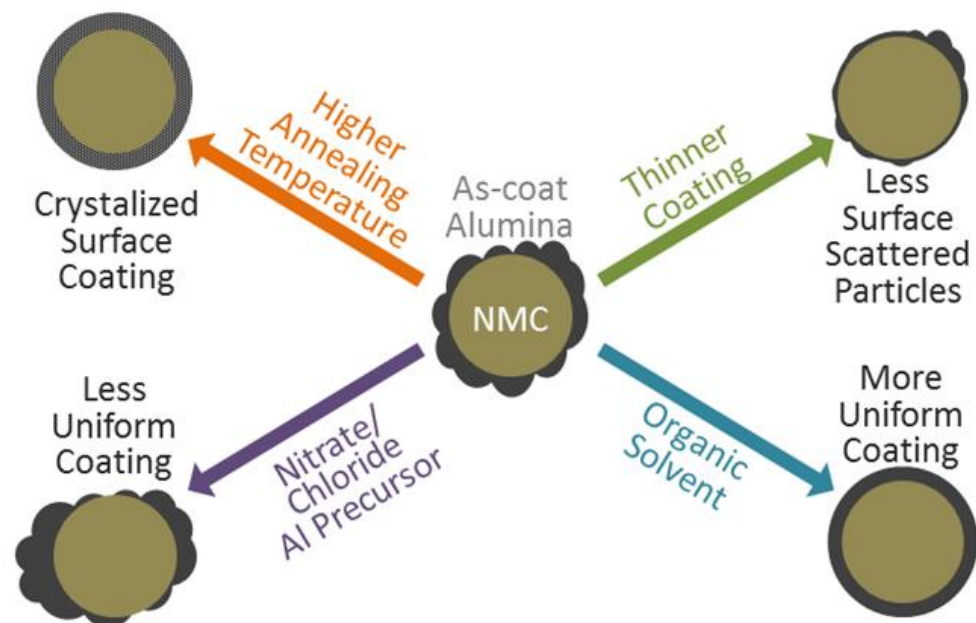Mass Normalized ^{7}Li NMR

(a) Al-N + H$_2$O
Al(NO$_3$)$_3$
As coat
Pristine
NMC532
400 °C 8 h
800 °C 8 h

(b) Al-N + MeOH
Al(NO$_3$)$_3$

(c) Al-I + MeOH
Al(isopropoxide)$_3$

Mass Normalized Intensity

Chemical Shift (ppm)

^{27}Al MAS NMR

γ-LiAlO$_2$ α-LiAlO$_2$ Al$_2$O$_3$ Al(OH)$_3$

Al-N + H$_2$O
800 °C 8 h
400 °C 8 h
As coat

Al-N + MeOH
800 °C 8 h
400 °C 8 h
As coat

Al-I + MeOH
800 °C 8 h
400 °C 8 h
As coat

Chemical Shift (ppm)

- **The aqueous coating** process causes lithium removal from bulk and formation of surface lithium bearing species

- **Oxidizing anions** of aluminum salts used corrode surface species

- **Non-aqueous coatings** lead to less Li extraction and surface lithium species

EFFECT OF SALT AND SOLVENT

Annealing T.

No annealing
400 °C
800 °C

Thickness

No coating
0.2wt%Al_2O_3
0.5wt%Al_2O_3
2wt%Al_2O_3

Solvent

No coating
H_2O
EOH
MeOH
Xylene

Salt

No coating
Al-N
Al-C
Al-I
Al-A

Axes for all plots: x = Discharge Capacity of the First C/10 Formation Cycle (mAh/g); y = Discharge Capacity after 80 C/3 Cycles (mAh/g)

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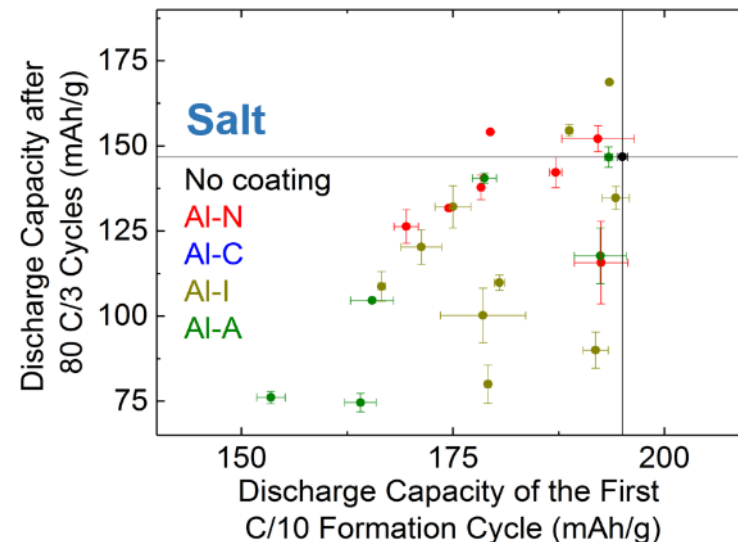
EFFECT OF SALT AND SOLVENT

Optimization of precursor, solvent, annealing condition and loading is critical for interface composition and effectiveness of the surface coating layers

FULL CELL CYCLING DATA

Baseline
Al/H$_2$O/Gen2
Al/H$_2$O/Gen2+TMSPi
Al/MeOH/Gen2
Al/MeOH/Gen2+TMSPi

Data from CAMP
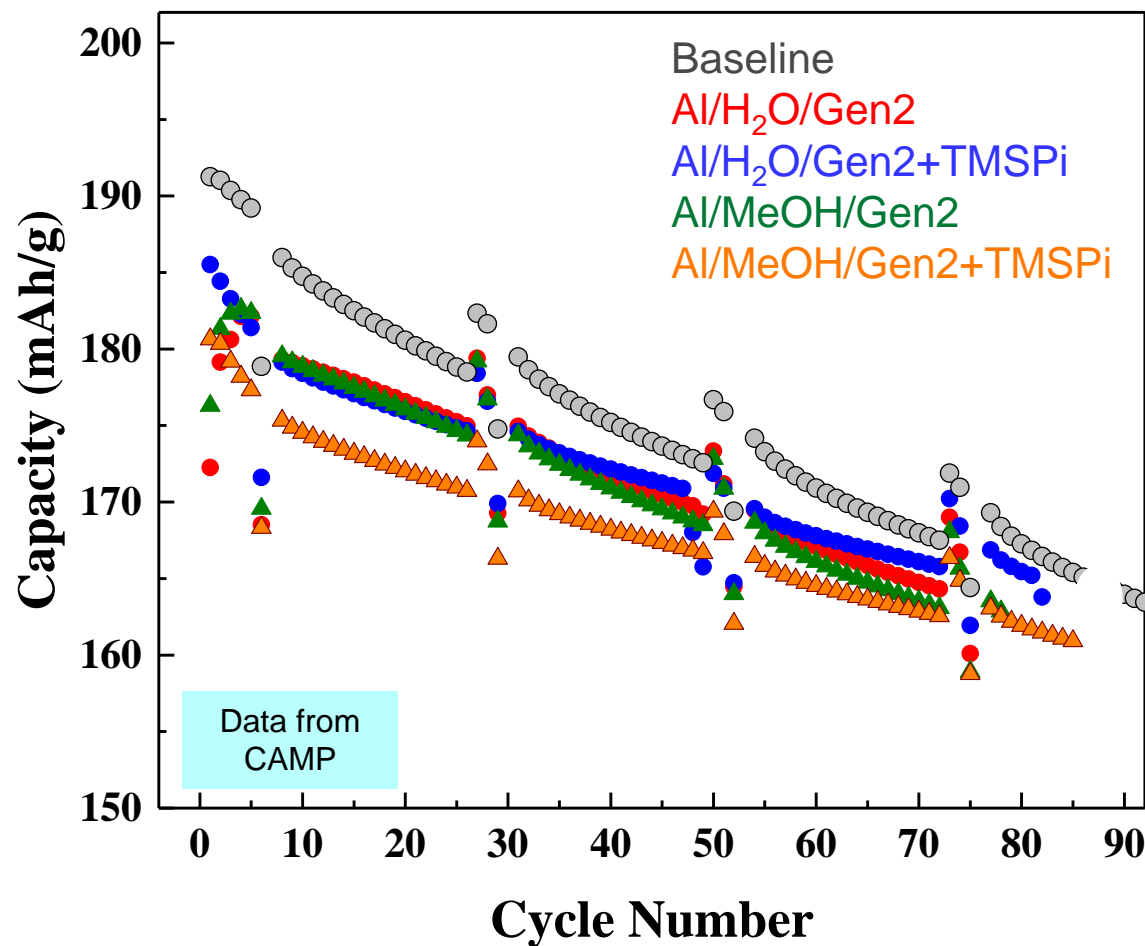
- Fade rate of alumina coated samples (slope) slightly improved over baseline

- Addition of additive in combination with Al treatment also slightly lowers fade rate and improves impedance (BAT252)

- Initial capacities lower for treated samples

HEHV Protocol: 30°C
C/3 Tap Charge to 1.5 V, 6 h OCV Rest
3.0-4.4 V: 4-C/10 cycles then [1-C/10 cycle, 1-C/3 Cycle, HPPC, 20-C/3 cycles with 3hr hold at top of charge] Bracketed Protocol Repeated 5x

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AVERAGE DISCHARGE CAPACITY RETENTION

Combinations of optimized Al_2O_3 coating processes and previously a proven additive (BAT252) leads to slight enhancements in cycle performance

NMC532 Type	Electrolyte	Average Discharge Capacity Retention (%)		
		At Cycle 46 (%)	# of Cells in Average	Retention Range at Cycle 46 (%)
Pristine (Baseline A-C015A)	**Gen 2**	**93.51 %**	5	91.9 - 95.7 %
WC Al_2O_3 with H_2O	Gen 2	94.75 %	4	94.7 - 94.8 %
WC Al_2O_3 with MeOH	Gen 2	94.35 %	4	94.2 - 94.5 %
WC Al_2O_3 with H_2O	1 week aged TMSPI	95.71 %	4	95.4 - 96.2 %
WC Al_2O_3 with MeOH	1 week aged TMSPI	95.59 %	3	95.5 - 95.7 %

❖ Discharge Capacity Retention is based off of the 9th cycle (2nd C/3 Cycle) and the 46th cycle (Latest Shared C/3 Cycle)

5:12:12 µL of Electrolyte
Celgard 2325 at 16 mm diameter
A12 Graphite (1.84 mAh/cm²) at 15 mm diameter
NMC532 Type at 14 mm diameter

HEHV Protocol: 30°C
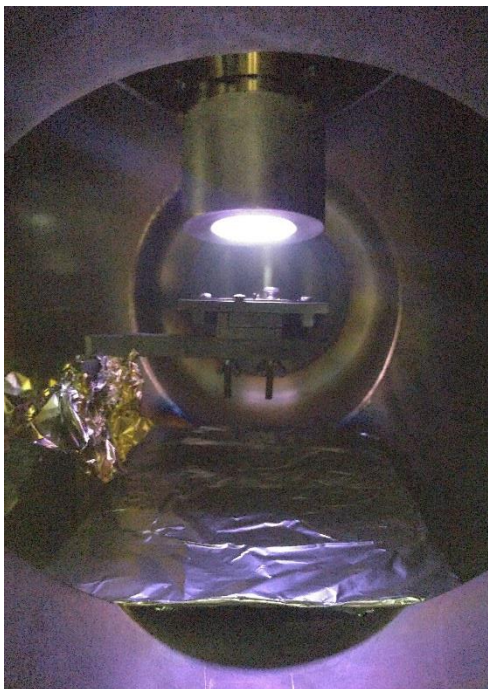C/3 Tap Charge to 1.5 V, 6 h OCV Rest
3.0-4.4 V: 4-C/10 cycles then
[1-C/10 cycle, 1-C/3 Cycle, HPPC, 20-C/3 cycles with 3hr hold at top of charge] Bracketed Protocol Repeated 5x
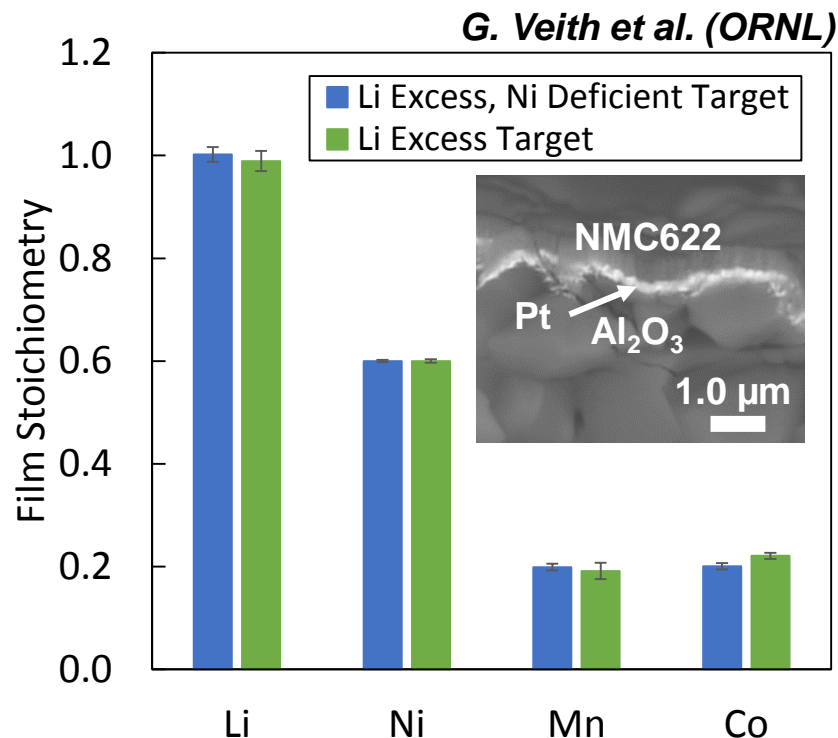
THIN FILM NMC CATHODES

Thin film cathodes isolate active materials from conductive additives and binder for fundamental studies of interfacial reactions.

G. Veith et al. (ORNL)

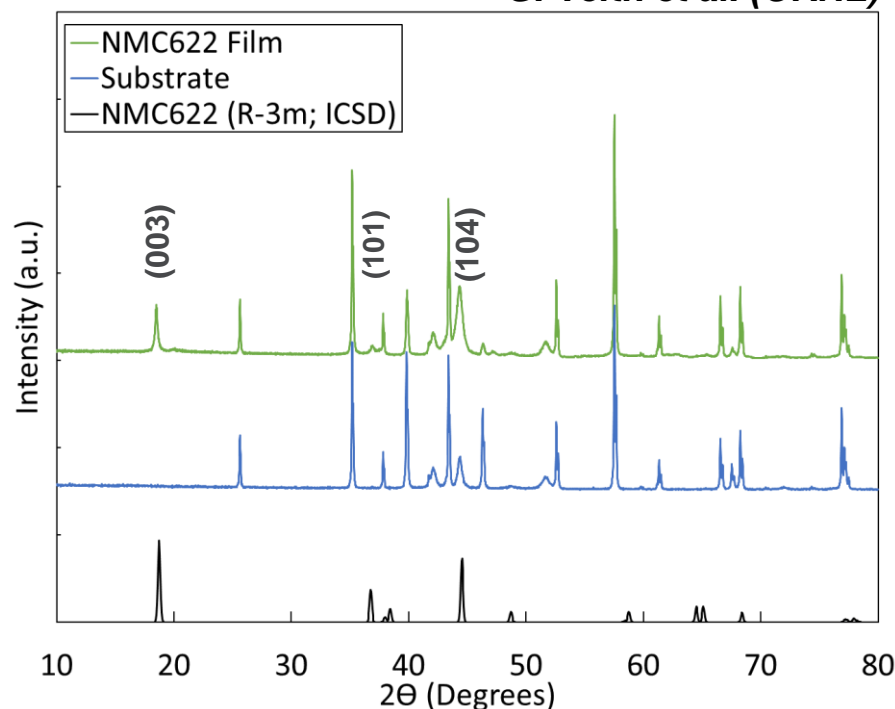RF magnetron sputtering deposits uniform cathode films with controlled thickness.

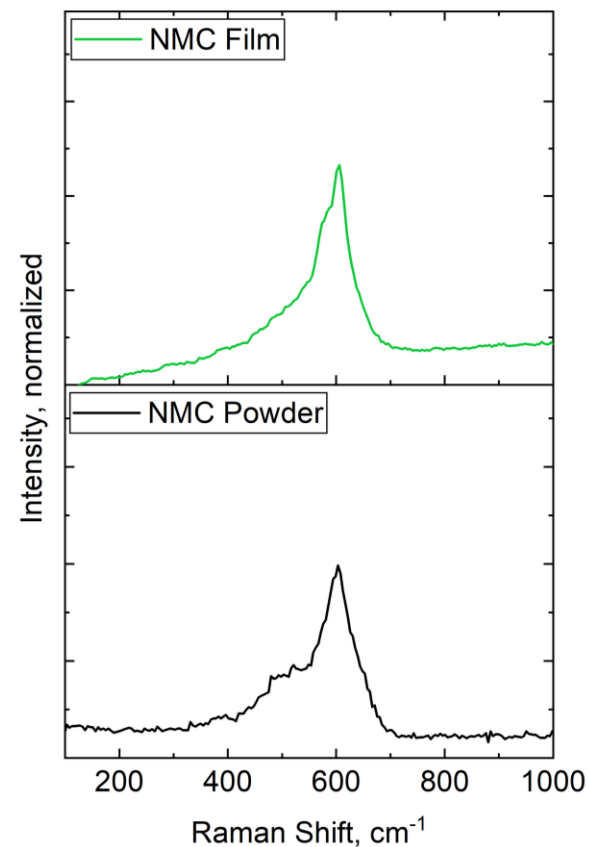ICP confirmed the desired stoichiometry for NMC622.

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THIN FILM NMC CATHODES

Processing conditions were systematically varied to obtain the desired phase and stoichiometry.
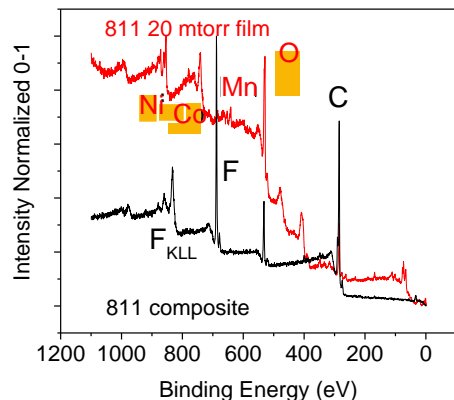
G. Veith et al. (ORNL)

XRD verifies formation of the desired layered phase for comparison to composite electrodes.

Raman micro-spectroscopy further confirms the films are homogenous and crystallize in the desired phase.
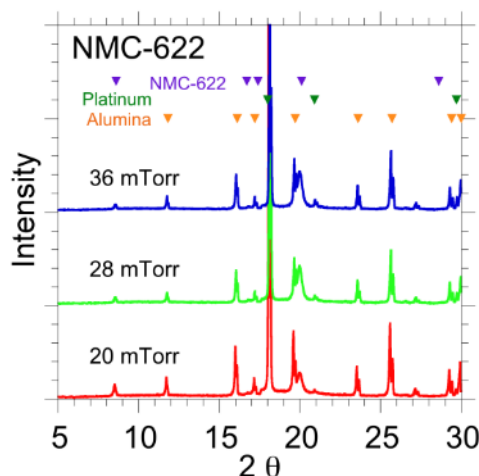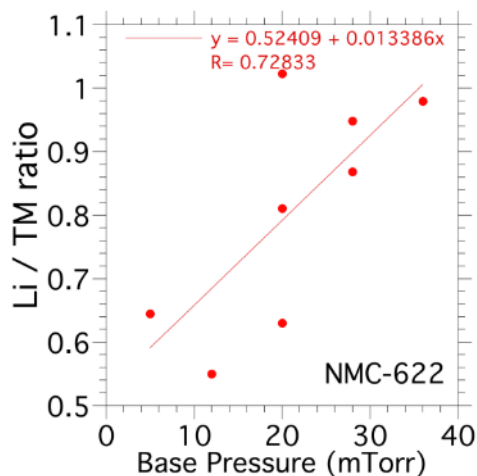
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THIN FILM NMC CATHODES

Magnetron sputtering can produce a thin film cathode structure that enables advanced characterization techniques that are not possible on conventional tape cast cathodes.
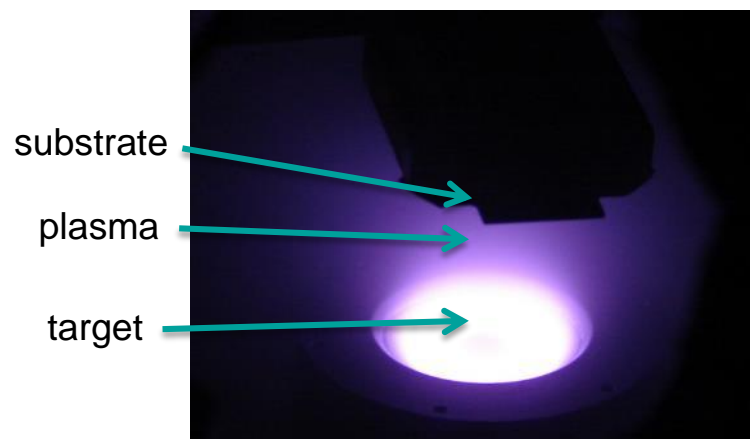
Magnetron sputtering in Argon

Example:
X-ray photoelectron spectroscopy (XPS) of an NMC thin film cathode has strong transition metal peaks. XPS of a tapecast NMC cathode is dominated by the binder and carbon additives.

substrate

plasma

target

G. Veith et al. (ORNL)

ICP-MS and XRD have been used to determine the phase & lithium content of the sputtered NMC cathode films.

SUMMARY

- A new interfacial relationship has been identified and experimentally observed. In this system, the top of the active NMC cathode (α-NaFeO$_2$ type) templates α-LiAlO$_2$ at the interface while above this α-LiAlO$_2$ layer, the remaining lithium aluminate transforms to the thermodynamically stable γ-LiAlO$_2$.

- Coating morphology tracks annealing temperature, weight percent, and extent of lithium species on the surface.

- Systematic studies of coating methods and materials were performed in half cell data then scaled up and tested by CAMP (ANL) in multiple full cells. Compared to the 532//Gr baseline, capacity fade rate was slightly improved using the optimal coating processes in combination with and without an aged-TMSPi additive.

FUTURE WORK

- Extend the evaluation of the optimized alumina based coatings identified and continue to work with the CAMP evaluation team and the HEHV Electrolyte Development Group. Identify and evaluate the synergies between the coated cathodes and various classes of new electrolyte additives identified.

- Working with the ORNL materials team, we will extend our coatings method to take into account the role of surface charge (Zeta potential). Initial studies indicate that high quality coatings are possible but more effort on non-aqueous systems is being discussed for the various metal oxides proposed.

- The role of annealing temperature and anti-site mixing phenomena for thin film cathodes of NMC622 will continue to be evaluated in association with the materials development team.

Any proposed future work is subject to change based on funding levels

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Materials Engineering Research Facility (MERF)
- Post-Test Facility (PTF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Advanced Photon Source (APS)
- Argonne Leadership Computing Facility (ALCF)

High-Energy/Voltage Project Contributors

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- David Wood
- Zhengcheng Zhang
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RESPONSES TO LAST YEARS COMMENTS

- **The presenters have examined and studied the fate of the aluminum species in the coating, but did not follow up this study with a solid discussion on the possible mechanisms**.

Thank you. We appreciate your comment and in a continuation of these studies we varied our synthetic methods and have done more with MAS-NMR and TEM capabilities to better understand the role of morphology and the method used to coat the sample, as reported in the slides herein. Yes, while alumina has been extensively studied, it is a very good testbed due to the spectroscopic handles it allows. We were able to show mechanistically that the fate of the coating (grain boundary phase vs lattice dopant) tracks the manganese content, the solvent used to solubilize the precursor, and the anion in the precursor salt. The stability and ultimate destination of the aluminum cations is related to the availability of lithium compounds on the surface.

- **It would be helpful to compare cycle life results of the materials synthesized in this program to commercially available materials.**

In our studies we start with commercially available samples (from CAMP team) and use them to develop working theories and approaches to understanding the aluminum species. Once established we use literature methods to create more custom samples to test our theories. For instance, varying the Mn content to track the environment of the Al. This year we were able to optimize the variables we identified to make a stable coating with the best performance – taking dozens of independent formulations to the best two and scaling them up to levels usable by the CAMP facility who evaluated them in a more rigorous study (included in our presentation).

- **How much knowledge gathered from single crystal can be used to address the challenges of the polycrystalline cathode materials.**

Thank you for the comment – we have continued these studies and extended the theory and modeling studies to help identify how the particular planes of the cathode may have different properties with regards to binder interactions and even catalytic activity with the electrolyte. These issues are discussed this year in more detail in the Modeling HEHV talk by our colleague Dr. Hakim Iddir.

BACKUP SLIDES

- Coatings with ALD-type chemistry
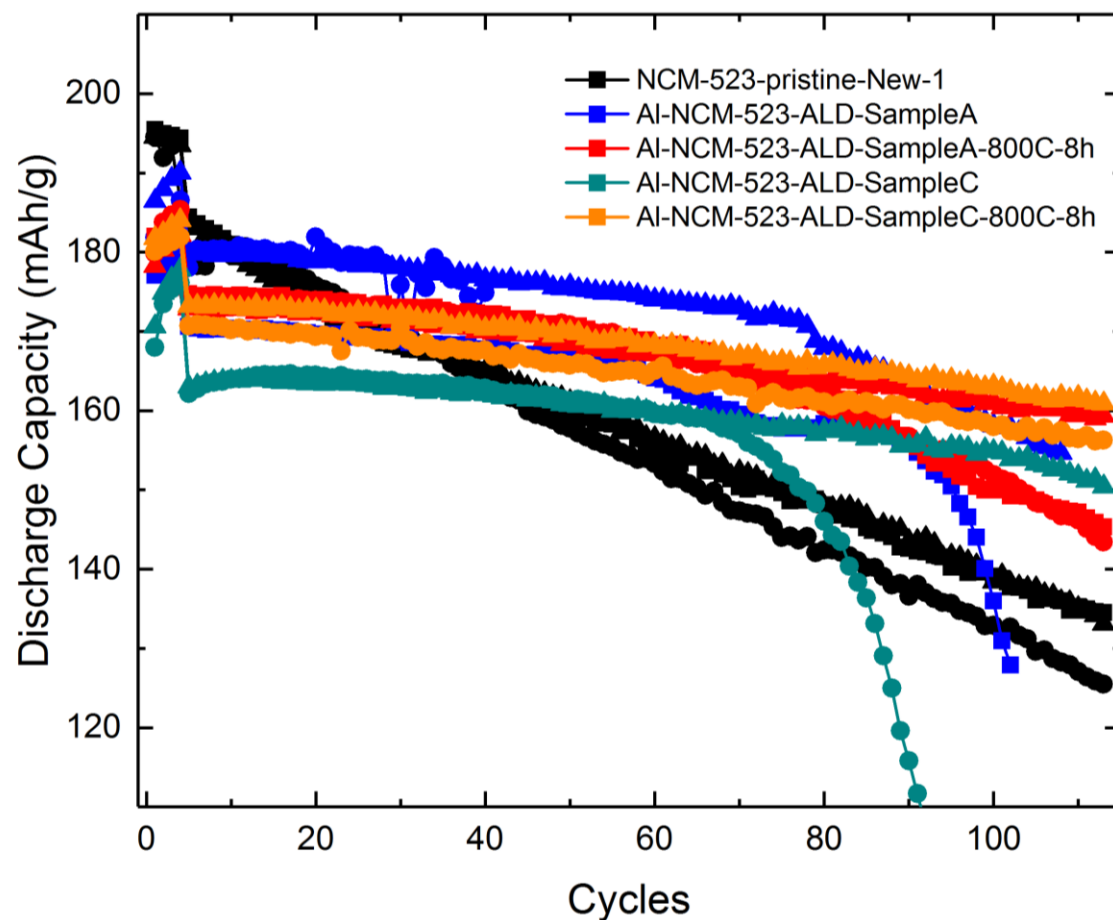- Cycling Data of various Salts

COATINGS BASED ON ALD-CHEMISTRY AS THE SOURCE OF SURFACE ALUMINA

- **More ALD chemistry cycles lead to rougher surfaces**
- **As-coated ALD chemistry samples show uneven amorphous coatings**
- **Annealing the ALD chemically coated samples at 800 $^\circ$C evens out and flattens the crystalline coatings**
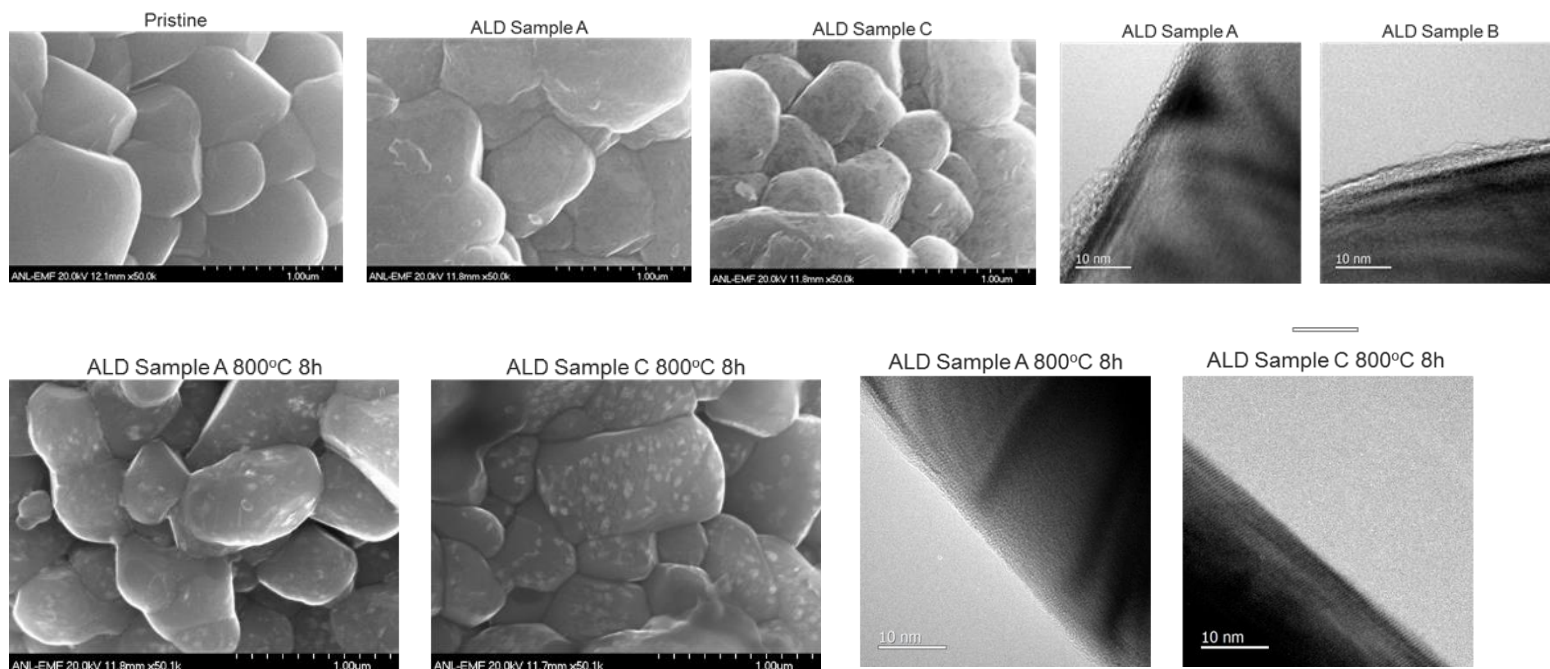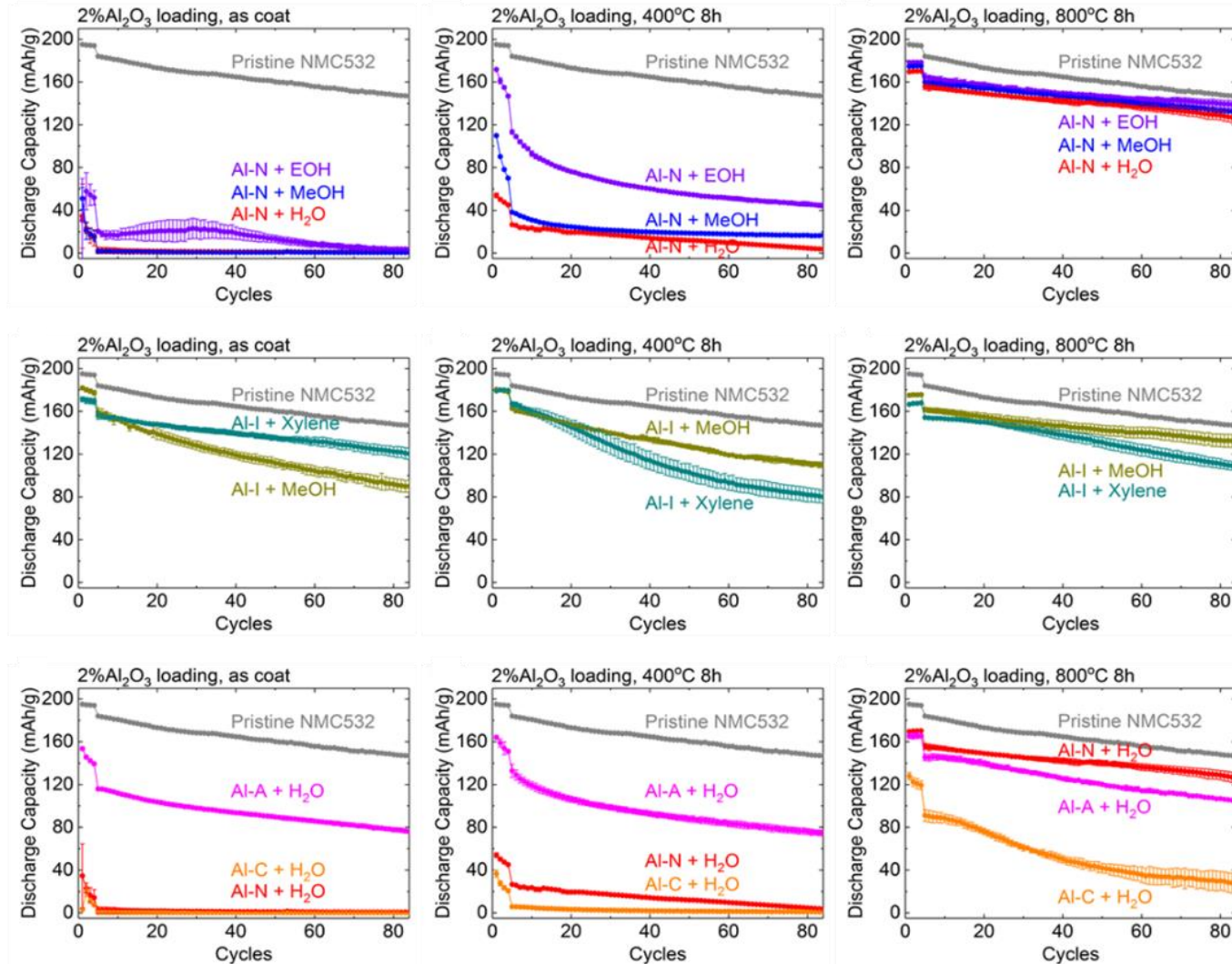
COATINGS BASED ON ALD-CHEMISTRY AS THE SOURCE OF SURFACE ALUMINA

- **Thicker ALD chemistry coatings lead to lower capacity before annealing**

- **Samples coated with ALD-chemistry show similar performance after annealing**

Legend:
- NCM-523-pristine-New-1
- Al-NCM-523-ALD-SampleA
- Al-NCM-523-ALD-SampleA-800C-8h
- Al-NCM-523-ALD-SampleC
- Al-NCM-523-ALD-SampleC-800C-8h

X-axis: Cycles
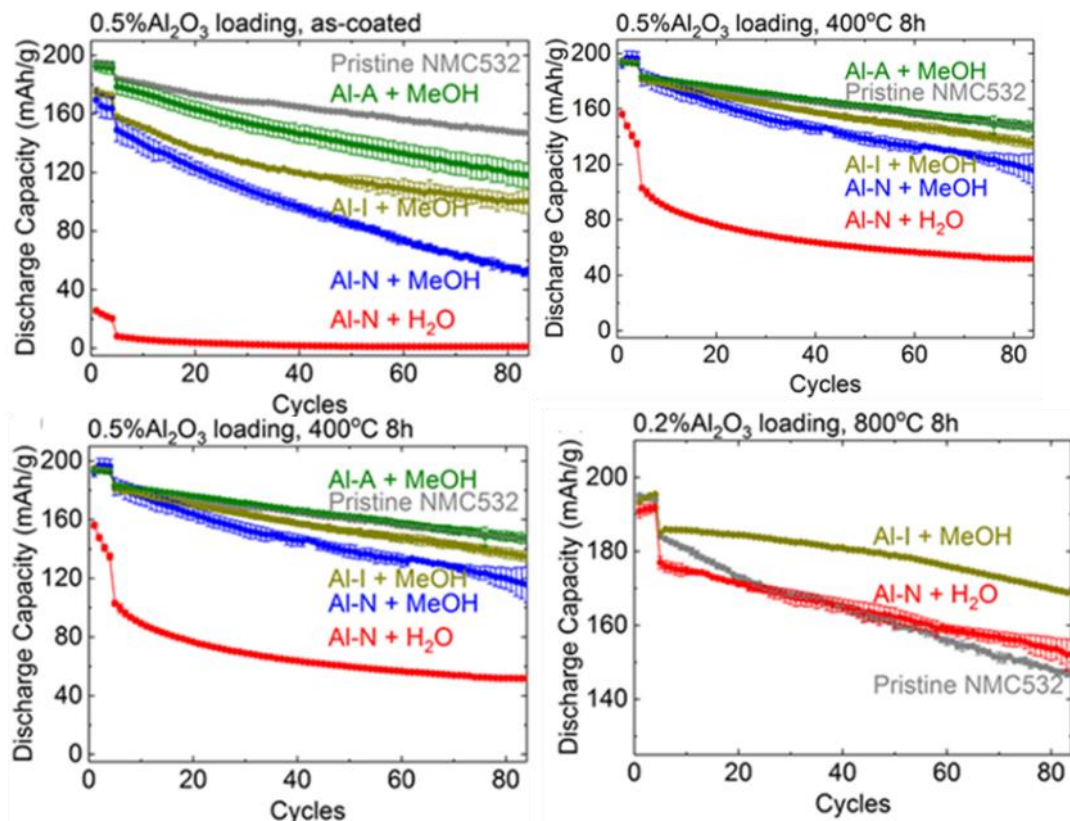Y-axis: Discharge Capacity (mAh/g)

CYCLING DATA

Effect of salt and solvent

Half-cell cycled between 3-4.5V, first at C/10 for 4 formation cycles, then at C/3 for 80 cycles. Error bars represent the standard derivation of three measurements for each sample.

CYCLING DATA

Effect of salt and solvent

- **Non-aqueous coating process shows higher initial capacities**
- **Al-N & Al-C leads to low capacity before annealing or after 400°C annealing**
- **Al-I & Al-A has less capacity improvement after annealing**
- **Most samples show similar capacity and cyclability after 800°C annealing**
- **Al-I + MeOH combination shows further improvement when lower the loading to 0.2%**